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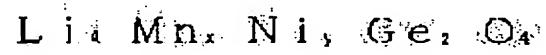
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(54) POSITIVE ELECTRODE ACTIVE MATERIAL FOR LITHIUM SECONDARY BATTERY

(57)Abstract:

PROBLEM TO BE SOLVED: To improve both discharge capacity and a charging-discharging cycle characteristic by composing positive electrode active material of a spinel type Li-Mn based compound oxide of a specific composition as a main component.

SOLUTION: The composition of this compound oxide is represented by the formula, where $0.05 \leq A \leq 2.3$, $X+Y+Z=2$, $Y+Z=0.02-0.04$, and the atom number ratio of Y to Z is 1:9-9:1, desirably $A=1$, $Y+Z=0.05-0.15$, and the atom number ratio Y:Z is 8.2-3:7. If $Y+Z$ being larger than 0.4, an impurity layer other than a spinel phase is apt to be generated. The compound oxide expressed by the formula is manufactured by heat-sintering a specified ratio of mixture of an oxide, a hydroxide, carbonate or nitrate composed of elements other than oxygen, at $500-1,000^{\circ}\text{C}$ for 1-50 hours in the atmosphere. Positive electrode active material may also be formed by using one or more kinds of compound oxide expressed by the formula, in combination with a small quantity of an Li-Mn compound oxide or an Li-Co compound oxide excluding the compound oxide expressed by the formula, if necessary.



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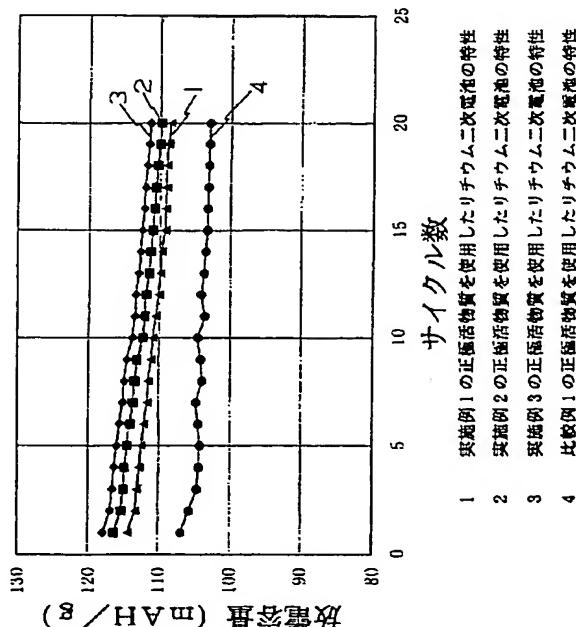
(54)【発明の名称】 リチウム二次電池用の正極活物質

(57)【要約】

【課題】 放電容量と充放電サイクル特性の両方に優れた二次電池の製造に有用なリチウム二次電池用の正極活物質を提案すること。

【解決手段】 一般式 $L_i \cdot Mn_x \cdot Ni_y \cdot Ge_z \cdot O$ (ここに、 $0.05 \leq A \leq 2.3$ 、 $X+Y+Z=2$ 、 Y と Z の合計量は $0.02 \sim 0.4$ 、 Y と Z との原子数比は $1:9 \sim 9:1$) を有するスピネル型 $L_i \cdot Mn$ 系複合酸化物を主成分とするリチウム二次電池用の正極活物質。

【効果】 各種の電気機器とりわけ携帯用品用の長寿命リチウム二次電池の製造に好適である。



【特許請求の範囲】

【請求項1】 一般式 $Li_xMn_xNi_xGe_xO$ (ここに、 $0.05 \leq A \leq 2.3$ 、 $X+Y+Z=2$ 、YとZの合計量は $0.02 \sim 0.4$ 、YとZとの原子数比は $1:9 \sim 9:1$) を有するスピネル型 $Li \cdot Mn$ 系複合酸化物を主成分とする特徴とするリチウム二次電池用の正極活物質。

【請求項2】 請求項1における一般式において、Aは1であり、YとZの合計量は $0.05 \sim 0.15$ であり、またYとZとの原子数比は8(Y) : 2(Z) ~ 3(Y) : 7(Z) である請求項1記載のリチウム二次電池用の正極活物質。

【発明の詳細な説明】

【0001】

【発明の属する技術分野】 本発明は、リチウム二次電池用の正極活物質に関し、特にスピネル型 $Li \cdot Mn$ 系複合酸化物を主成分とするリチウム二次電池用の正極活物質に関する。

【0002】

【従来の技術】 リチウム二次電池は、起電力並びにエネルギー密度の点で優れているので一般的に益々注目されつつあり、斯界では一層実用性の高い製品を開発する目的で各種の改善研究が鋭意なされている。正極活物質の改善研究もその重要な一つである。正極活物質として、従来のリチウムと遷移金属元素との複合酸化物 ($LiMeO$ 、Meは周期律表の新9~10族遷移金属元素) に代わって、一層の高起電力が得られるスピネル型の $Li \cdot Mn$ 複合酸化物 (Li_xMn_xO) が近時提案されており、該複合酸化物においてAの値が $0.05 \sim 0.5$ の場合には4V級の、またAの値が $0.5 \sim 1.1$ の場合には3V級のリチウム二次電池が得られることが知られている。

【0003】 ところで該 $Li \cdot Mn$ 複合酸化物を正極活物質として用いた二次電池は、概して充放電サイクル特性に問題がある。即ち、充放電のサイクルを行うと電池*

$Li_xMn_xNi_xGe_xO$
(ここに、 $0.05 \leq A \leq 2.3$ 、 $X+Y+Z=2$ 、YとZの合計量は $0.02 \sim 0.4$ 、YとZとの原子数比は $1:9 \sim 9:1$)。

【0008】 (1)式において、A値が 0.05 未満の場合や 2.3 より大の場合には放電容量が低下する問題がある。YとZの合計量が 0.02 未満であると、放電容量と充放電サイクル特性の改善効果が少なく、 0.4 より多いとスピネル相以外の不純物相が生成し易くなつて放電容量が減少する。したがってYとZとの合計量は、 $0.03 \sim 0.3$ の範囲、特に $0.05 \sim 0.15$ の範囲であることが好ましい。YとZとの原子数比において、Yの原子数がZのそれに対して過大であると放電容量の改善効果が少なく、一方、Yの原子数がZのそれに対して過少であると充放電サイクル特性の改善効果が

*の放電容量が急激に低下する。この問題を改善するためには、Mnの一部をCo、Cr、Ni、Feなどの元素で置換することが提案されている。しかしかかる提案は、電池の充放電サイクル特性の改善には効果的ではあっても正極活物質の単位重量あたりの放電容量が大幅に低下する新たな問題を惹起する。

【0004】

【発明が解決しようとする課題】 しかして本発明は、放電容量と充放電サイクル特性の両方に優れたリチウム二次電池の製造に有用な正極活物質を提案することを課題とする。

【0005】

【課題を解決するための手段】 上記の課題は、つぎのリチウム二次電池用の正極活物質により解決することができる。

(1) 一般式 $Li_xMn_xNi_xGe_xO$ (ここに、 $0.05 \leq A \leq 2.3$ 、 $X+Y+Z=2$ 、YとZの合計量は $0.02 \sim 0.4$ 、YとZとの原子数比は $1:9 \sim 9:1$) を有するスピネル型 $Li \cdot Mn$ 系複合酸化物を主成分とすることを特徴とするリチウム二次電池用の正極活物質。

(2) 上記(1)における一般式において、Aは1であり、YとZの合計量は $0.05 \sim 0.15$ であり、またYとZとの原子数比は8(Y) : 2(Z) ~ 3(Y) : 7(Z) である上記(1)記載のリチウム二次電池用の正極活物質。

【0006】

【作用】 スピネル型 $Li \cdot Mn$ 系複合酸化物のMn一部を、NiとGeとで且つ上記する特定量範囲で置換したものを正極活物質として使用することにより上記の課題を解決することができる。

【0007】

【発明の実施の形態】 本発明で採用するスピネル型 $Li \cdot Mn$ 系複合酸化物は、つぎの一般式(1)を有する、

$Li_xMn_xNi_xGe_xO$
(1)
少なくなる。したがってYとZとの原子数比は、8(Y) : 2(Z) ~ 3(Y) : 7(Z) の範囲、特に7(Y) : 3(Z) ~ 4(Y) : 6(Z) の範囲であることが好ましい。

【0009】 好ましいスピネル型 $Li \cdot Mn$ 系複合酸化物を例示すると、 $Li(Mn_{1.9}Ni_{0.1}Ge_{0.02})O$ 、 $Li(Mn_{1.9}Ni_{0.1}Ge_{0.04})O$ 、 $Li(Mn_{1.9}Ni_{0.1}Ge_{0.05})O$ 、 $Li(Mn_{1.9}Ni_{0.1}Ge_{0.06})O$ 、 $Li(Mn_{1.9}Ni_{0.1}Ge_{0.08})O$ などである。

【0010】 一般式(1)で示されるスピネル型 $Li \cdot Mn$ 系複合酸化物は、一般的にはそれを構成する酸素以外の元素、即ち Li 、 Mn 、 Ni 、および Ge の酸化物、水酸化物、炭酸塩、硝酸塩などを各元素の原子数比

が(1)式で示される割合となるように混合し、得られた混合物を大気中で500～1000°Cで1～50時間加熱焼成することにより製造することができる。例えば、Mn原料として電解MnO₂(EMD)を、Li原料としてLi₂CO₃やLiOH·H₂Oを、Ni原料としてNi(OH)₂を、またGe原料としてGeO₂をそれぞれ用い、ついでそれらの原料を所望の量比で混合し、得られた混合物を750°C前後で約15時間加熱焼成することにより製造することができる。また従来周知のLi₂MnO₃のMnの一部をNiのみで置換した複合酸化物とGeO₂などのGe原料との混合物を大気中で500～1000°Cで1～50時間加熱焼成することによっても製造することができる。

【0011】本発明の正極活物質は、一般式(1)で示されるスピニル型Li₂Mn系複合酸化物の一種または二種以上の組みからなっていてもよく、必要に応じて他の正極活物質、例えば一般式(1)で示されるスピニル型Li₂Mn系複合酸化物以外の各種のLi₂Mn系複合酸化物、Li₂CO₃系複合酸化物などの少量(例えば一般式(1)で示されるスピニル型Li₂Mn系複合酸化物100重量部あたり0.1～10重量部程度)と併用してもよい。

【0012】本発明の正極活物質は、従来のLi₂Mn系複合酸化物を正極活物質とする非水電解質リチウム二次電池や固体電解質リチウム二次電池などの分野で従来から知られている方法と同じ方法にて実用することができる。以下に、その代表的乃至好ましい実用方法の若干例を説明する。

【0013】正極活物質の結着剤としては、ポリテトラフルオロエチレン、ポリビニリデンフルオリド、ポリエチレン、エチレン-プロビレン-ジエン系ポリマーなどが例示され、導電剤としては、各種導電性黒鉛や導電性カーボンブラックなどが例示される。

【0014】正極活物質の使用量は、正極活物質、結着剤、および導電剤の合計量100重量部あたり80～95重量部程度であり、結着剤の使用量は正極活物質100重量部あたり1～10重量部程度であり、また導電剤の使用量は正極活物質100重量部あたり3～15重量部程度である。

【0015】正極シートは、正極集電体の片面または両面に正極活物質、結着剤、および導電剤からなる混合組成物を塗布し、充分に乾燥後、圧延して形成することができ、片面または両面に厚さ20～500μm程度、特に50～200μm程度の正極活物質層を有するものが例示される。

【0016】本発明の正極活物質と共に用いられる負極活物質として好ましい例を挙げると、各種の天然黒鉛や人造黒鉛、例えば纖維状黒鉛、鱗片状黒鉛、球状黒鉛などの黒鉛類であり、その結着剤としては、ポリテトラフルオロエチレン、ポリビニリデンフルオリド、ポリエチレ

ン、エチレン-プロビレン-ジエン系ポリマーなどである。負極活物質の使用量は、負極活物質と結着剤との合計量100重量部あたり80～96重量部程度である。

【0017】正極集電体としては、アルミニウム、アルミニウム合金、チタンなどの導電性金属の、厚さ10～100μm程度、特に15～50μm程度の箔や穴あき箔、厚さ25～300μm程度、特に30～150μm程度のエキスバンドメタルなどが好ましい。負極集電体としては、銅、ニッケル、銀、SUSなどの導電性金属の、厚さ5～100μm程度、特に8～50μm程度の箔や穴あき箔、厚さ20～300μm程度、特に25～100μm程度のエキスバンドメタルなどが好ましい。

【0018】非水電解質としては、塩類を有機溶媒に溶解させた電解液が例示される。該塩類としては、LiClO₄、LiBF₄、LiPF₆、LiAsF₆、LiAlCl₄、Li(CF₃SO₂)₂Nなどが例示され、それらの一種または二種以上の混合物が使用される。

【0019】有機溶媒としては、エチレンカーボネート、プロピレンカーボネート、ジメチルカーボネート、ジエチルカーボネート、エチルメチルカーボネート、ジメチルスルホキシド、スルホラン、ヤープチロラクトン、1,2-ジメトキシエタン、N,N-ジメチルホルムアミド、テトラヒドロフラン、1,3-ジオキソラン、2-メチルテトラヒドロフラン、ジエチルエーテルなどが例示され、それらの一種または二種以上の混合物が使用される。また電解液中における上記塩類の濃度は、0.1～3モル/リットル程度が適当である。

【0020】

【実施例】以下、実施例により本発明を一層詳細に説明するとともに、比較例をも挙げて本発明の顕著な効果を示す。以下において%、部とあるは、いずれも重量%、重量部を意味する。

【0021】実施例1

Mn原料として電解MnO₂を78.2%、Li原料としてLi₂CO₃を17.45%、Ni原料としてNi(OH)₂を3.51%、またGe原料としてGeO₂を0.84%それぞれ用い、ついでそれらの原料をよく混合し、得られた混合物を約750°Cで約15時間焼成し、ついで粉碎して、Li₂(Mn_{1.9}Ni_{0.05}Ge_{0.05})O₂の化学式を有するスピニル型Li₂Mn系複合酸化物からなる微粉末の正極活物質を得た。

【0022】実施例2

Mn原料として電解MnO₂を78.2%、Li原料としてLi₂CO₃を17.49%、Ni原料としてNi(OH)₂を2.63%、またGe原料としてGeO₂を1.68%それぞれ用い、ついでそれらの原料をよく混合し、得られた混合物を約750°Cで約15時間焼成し、ついで粉碎して、Li₂(Mn_{1.9}Ni_{0.05}Ge_{0.05})O₂の化学式を有するスピニル型Li₂Mn系

複合酸化物からなる微粉末の正極活物質を得た。

【0023】実施例3

Mn原料として電解MnO₂を78.22%、Li原料としてLi₂CO₃を17.49%、Ni原料としてNi(OH)₂を2.19%、またGe原料としてGeO₂を2.1%それぞれ用い、ついでそれらの原料をよく混合し、得られた混合物を約750°Cで約15時間焼成し、ついで粉碎して、Li₂(Mn_{1.99}Ni_{0.01}Ge_{0.01})O₄の化学式を有するスピネル型Li₂·Mn系複合酸化物からなる微粉末の正極活物質を得た。

【0024】比較例1

Mn原料として電解MnO₂を78.14%、Li原料としてLi₂CO₃を17.47%、またNi原料としてNi(OH)₂を4.39%それぞれ用い、ついでそれらの原料をよく混合し、得られた混合物を約750°Cで約15時間焼成し、ついで粉碎して、Li₂(Mn_{1.99}Ni_{0.01})O₄のスピネル型Li₂·Mn系複合酸化物からなる微粉末の正極活物質を得た。

【0025】実施例1～3および比較例1の各正極活物質（いずれも330メッシュのタイラー篩を通過した微粒子）を使用して、正極活物質92部、アセチレンブラック3部、ポリフッ化ビニリデン5部、およびN-メチル2ピロリドン70部とを混合してスラリーとした。このスラリーをアルミニウム箔上に塗布し乾燥して、20mg/cm²の正極活物質を有する正極シートを作製した。かくして得た各正極シートとLi箔とを多孔質ポリエチレンセバレータを介して密着対向させ、エチレンカーボネートとエチルメチルカーボネートとの混合溶媒（混合体積比率は1:1）1リットルあたり1モルのLiPF₆を溶解してなる溶液を電解液として使用して、これを上記正極シートとLi箔との間に含浸して密閉コイン型のリチウム二次電池を作製した。

【0026】各リチウム二次電池につき、下記に示す試験方法にて充放電サイクル試験を行った。その結果を図1に示す。図1において、1～3は、それぞれ実施例1～3の各正極活物質を使用した各リチウム二次電池の特性であり、4は比較例1の正極活物質を使用したリチウ

ム二次電池の特性である。

【0027】充放電サイクル試験方法：20°Cにおいて、正極シートの面積1cm²あたり1mAの定電流および4.3Vの定電圧下で5時間充電し、ついで正極シートの面積1cm²あたり0.5mAの定電流のもとで端子電圧が3Vとなる時点まで放電させ、この後1時間充放電を休止する。以上の充放電並びに休止を1サイクルとして20回繰り返す。各サイクルにおける放電容量は、放電電流値と放電時間から電気量(mA·H)を算出し、リチウム二次電池中に含まれている正極活物質の重量(g)から放電容量(mA·H/g)を得る。

【0028】図1から、実施例1～3の各正極活物質を使用したいずれのリチウム二次電池とも、比較例1の正極活物質を使用したリチウム二次電池と対比して、20回の充放電サイクルにおいて大きな放電容量を維持していることがわかる。

【0029】

【発明の効果】本発明の正極活物質は、従来のLi·Mn系複合酸化物からなる正極活物質と比較して高い放電容量を示し、しかも充放電サイクル特性にも極めて優れている。したがって本発明の正極活物質は、各種の電気機器とりわけ携帯用品用の長寿命リチウム二次電池の製造に好適である。

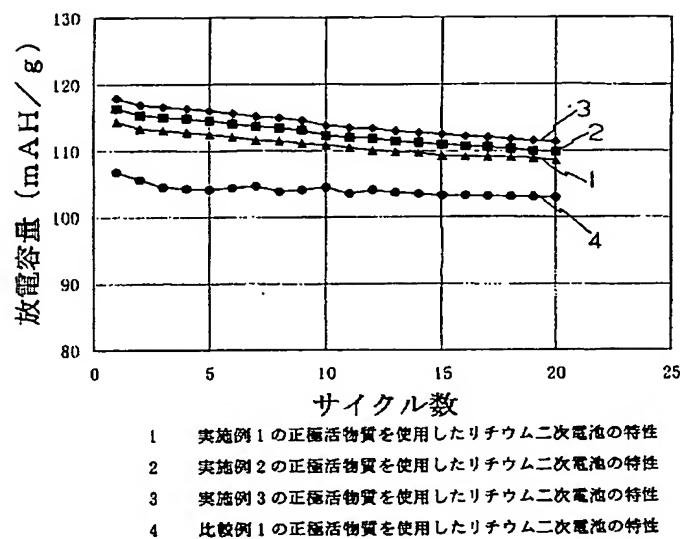
【図面の簡単な説明】

【図1】本発明の実施例1～3および比較例1の各正極活物質を使用した各リチウム二次電池の充放電サイクル特性を示すグラフである。

【符号の説明】

- 1 実施例1の正極活物質を使用したリチウム二次電池の特性である。
- 2 実施例2の正極活物質を使用したリチウム二次電池の特性である。
- 3 実施例3の正極活物質を使用したリチウム二次電池の特性である。
- 4 比較例1の正極活物質を使用したリチウム二次電池の特性である。

【図1】



JAPANESE

[JP,11-191416,A]

AA

CLAIMS DETAILED DESCRIPTION TECHNICAL FIELD PRIOR ART EFFECT OF THE INVENTION
TECHNICAL PROBLEM MEANS OPERATION EXAMPLE DESCRIPTION OF DRAWINGS DRAWINGS

[Translation done.]

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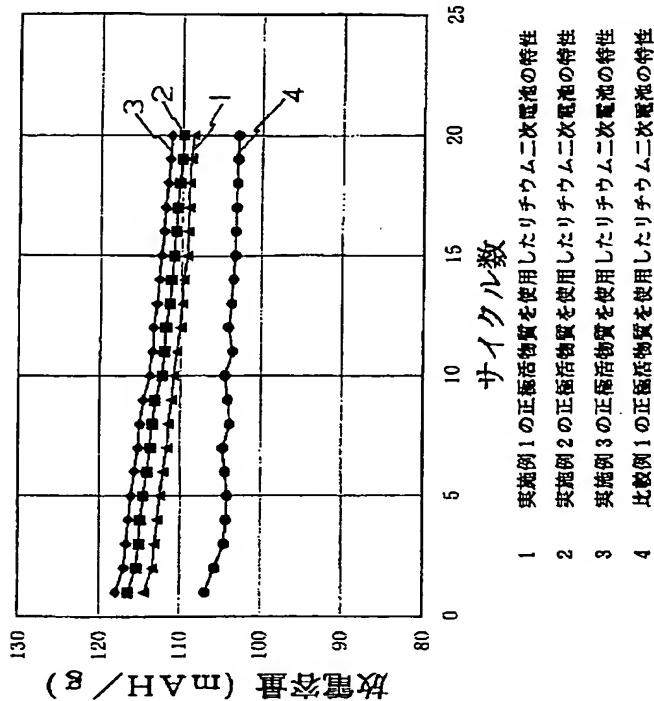
CLAIMS

[Claim(s)]

[Claim 1] The positive active material for lithium secondary batteries characterized by making into a principal component the spinel type Li-Mn system multiple oxide which has a general formula $\text{Li}_A \text{Mn}_x \text{Ni}_y \text{Ge}_z \text{O}_4$ (the atomic ratio of 0.02 to 0.4, and Y and Z is 1:9-9:1 here for the total quantity of $0.05 \leq A \leq 2.3$, $X+Y+Z=2$, and Y and Z).

[Claim 2] the general formula in a claim 1 -- setting -- A -- 1 -- it is -- the total quantity of Y and Z -- 0.05-0.15 -- it is -- moreover, the atomic ratio of Y and Z -- 8(Y): -- 2 (Z) - 3(Y): -- the positive active material for lithium secondary batteries according to claim 1 which is 7 (Z)

[Translation done.]

Drawing selection [Representative drawing] 

[Translation done.]

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[The technical field to which invention belongs] Especially this invention relates to the positive active material for lithium secondary batteries which makes a principal component a spinel type Li-Mn system multiple oxide about the positive active material for lithium secondary batteries.

[0002]

[Description of the Prior Art] Generally the lithium secondary battery is attracting attention all the more because it is excellent in respect of electromotive force and the energy density, and various kinds of improvement researches for the purpose which develops a product with still higher practicality are made wholeheartedly in the field. Improvement research of a positive active material is also the one [important]. the multiple oxide (LiMeO₂ --) of the conventional lithium as a positive active material, and a transition-metals element Instead of the new 9-10 group transition-metals element of a periodic table, as for Me, the spinel type Li-Mn multiple oxide (LiA Mn 2O₄) from which much more high electromotive force is obtained is proposed recently. When the values of A are 0.05-0.5 in this multiple oxide and 4V class and the value of A are 0.5-1.1, it is known that a 3V class lithium secondary battery will be obtained.

[0003] By the way, the rechargeable battery using this Li-Mn multiple oxide as a positive active material has a problem in a charge-and-discharge cycle property generally. That is, if the cycle of charge and discharge is performed, the service capacity of a cell will fall rapidly. In order to improve this problem, replacing a part of Mn by elements, such as Co, Cr, nickel, and Fe, is proposed. However, even if this proposal is effective for an improvement of the charge-and-discharge cycle property of a cell, the new problem to which the service capacity per unit weight of a positive active material falls sharply is caused.

[0004]

[Problem(s) to be Solved by the Invention] Carrying out a deer, this invention makes it a technical problem to propose a useful positive active material to manufacture of the lithium secondary battery excellent in both service capacity and the charge-and-discharge cycle property.

[0005]

[Means for Solving the Problem] The above-mentioned technical problem is solvable with the positive active material for the following lithium secondary batteries.

(1) The positive active material for lithium secondary batteries characterized by making into a principal component the spinel type Li-Mn system multiple oxide which has a general formula LiA Mn_x Ni_y Ge_z O₄ (the atomic ratio of 0.02 to 0.4, and Y and Z is 1:9-9:1 here for the total quantity of 0.05<=A<=2.3, X+Y+Z=2, and Y and Z).

(2) the above (1) the general formula which can be set -- setting -- A -- 1 -- it is -- the total quantity of Y and Z -- 0.05-0.15 -- it is -- moreover, the atomic ratio of Y and Z -- 8(Y): -- 2 (Z) - 3(Y): -- the above (1) which is 7 (Z) Positive active material for the lithium secondary batteries of a publication.

[0006]

[Function] The above-mentioned technical problem is solvable by using what was replaced in the amount range of specification which is with nickel and germanium and describes above Mn of a spinel type Li-Mn system multiple oxide part as a positive active material.

[0007]

[Embodiments of the Invention] The spinel type Li-Mn system multiple oxide adopted by this invention has the following general formula (1). LiA Mn_x Ni_y Ge_z O₄ (1)

(For the total quantity of 0.05<=A<=2.3, X+Y+Z=2, and Y and Z, the atomic ratio of 0.02 to 0.4, and Y and Z is 1:9-9:1 here).

[0008] (1) In an adult case, in a formula, there is a problem to which service capacity falls from the case where A value is less than 0.05, or 2.3. If [than 0.4] more [there are few improvement effects of service capacity and a charge-and-discharge cycle property that the total quantity of Y and Z is less than 0.02 and], it will become easy to

generate impurity phases other than a spinel phase, and service capacity will decrease. Therefore, as for the total quantity of Y and Z, it is desirable the range of 0.03-0.3 and that it is especially the range of 0.05-0.15. In the atomic ratio of Y and Z, to it of Z, the improvement effect of service capacity has few atomic numbers of Y as it is excessive, and on the other hand, the atomic number of the improvement effect of a charge-and-discharge cycle property of Y decreases as too little to it of Z. therefore, the atomic ratio of Y and Z -- 8(Y): -- 2 (Z) - 3(Y): -- the range of 7 (Z) -- especially -- 7(Y): -- 3 (Z) - 4(Y): -- it is desirable that it is the range of 6 (Z) [0009] if a desirable spinel type Li-Mn system multiple oxide is illustrated -- Li(Mn1.90nickel0.08germanium0.02) O4, Li(Mn1.90nickel0.06germanium0.04) O4, and Li (Mn1.90nickel0.05germanium0.05) -- O4, Li (Mn1.92nickel0.06germanium0.02) O4, and Li(Mn1.92nickel0.05germanium0.03) O4 etc. -- it is .

[0010] Generally, the spinel type Li-Mn system multiple oxide shown by the general formula (1) can mix elements other than the oxygen which constitutes it, i.e., the oxide of Li, Mn, nickel, and germanium, a hydroxide, a carbonate, a nitrate, etc. so that the atomic ratio of each element may serve as a rate shown by (1) formula, and it can manufacture them by carrying out heating baking of the obtained mixture at 500-1000 degrees C in the atmosphere for 1- 50 hours. For example, it is Li₂ CO₃ considering electrolysis MnO₂ (EMD) as a Li raw material as a Mn raw material. Considering LiOH-H₂ O as a nickel raw material, it is nickel (OH)₂. Moreover, using GeO respectively as a germanium raw material, subsequently, it can mix by the quantitative ratio of a request of those raw materials, and can manufacture by carrying out heating baking of the obtained mixture before and after 750 degrees C for about 15 hours. Moreover, LiA Mn 2O₄ of the conventional common knowledge It can manufacture also by carrying out heating baking of the mixture of the multiple oxide which replaced a part of Mn only with nickel, and germanium raw materials, such as GeO, at 500-1000 degrees C in the atmosphere for 1 to 50 hours.

[0011] The positive active material of this invention may consist of a kind of the spinel type Li-Mn system multiple oxide shown by the general formula (1), or two sorts or more. Various kinds of Li-Mn system multiple oxides other than the spinel type Li-Mn system multiple oxide shown by other positive active materials (1), for example, a general formula, if needed, You may use together with small quantity (for example, per [0.1] spinel type Li-Mn system multiple-oxide 100 weight section - 10 weight sections grade which are shown by the general formula (1)), such as a Li-Co system multiple oxide.

[0012] The positive active material of this invention can use the conventional Li-Mn system multiple oxide by the same method as the method learned for fields made into a positive active material, such as a nonaqueous electrolyte lithium secondary battery and a solid electrolyte lithium secondary battery, from the former. Below, the example of some of the typical or desirable practical use method is explained.

[0013] As a binder of a positive active material, polytetrafluoroethylene, poly vinylidene fluoride, polyethylene, and ethylene-propylene-diene system polymer etc. is illustrated, and various conductive graphites, conductive carbon black, etc. are illustrated as an electric conduction agent.

[0014] The amount of the positive active material used is per [80] total quantity 100 weight section of a positive active material, a binder, and an electric conduction agent - 95 weight sections grade, and the amount of the binder used is per [1] positive-active-material 100 weight section - 10 weight sections grade, and the amount of the electric conduction agent used is per [3] positive-active-material 100 weight section - 15 weight sections grade.

[0015] A positive-electrode sheet applies the mixed constituent which becomes one side or both sides of a positive-electrode charge collector from a positive active material, a binder, and an electric conduction agent, fully, after dryness, it can roll out and form and what has an about 50-200-micrometer positive-active-material layer especially about 20-500 micrometers in thickness to one side or both sides is illustrated.

[0016] When an example desirable as a negative-electrode active material shared with the positive active material of this invention is given, it is graphites, such as a various kinds of natural-graphites and artificial graphites, for example, fibrous graphite, and scale-like graphite and a nodular graphite, and is polytetrafluoroethylene, poly vinylidene fluoride, polyethylene, and ethylene-propylene-diene system polymer etc. as the binder. The amount of the negative-electrode active material used is per [80] total quantity 100 weight section - 96 weight sections grade of a negative-electrode active material and a binder.

[0017] Especially especially as a positive-electrode charge collector, an about 30-150-micrometer expanded metal etc. is desirable about 25-300 micrometers in about 15-50-micrometer a foil and a fenestrate foil, and thickness about 10-100 micrometers in thickness of conductive metals, such as aluminum, an aluminium alloy, and titanium. Especially especially as a negative-electrode charge collector, an about 25-100-micrometer expanded metal etc. is desirable about 20-300 micrometers in about 8-50-micrometer a foil and a fenestrate foil, and thickness about 5-100 micrometers in thickness of conductive metals, such as copper, nickel, silver, and SUS.

[0018] As nonaqueous electrolyte, the electrolytic solution which dissolved salts in the organic solvent is illustrated. As these salts, LiClO₄, LiBF₄, LiPF₆, LiAsF₆, LiAlCl₄, Li(CF₃ SO₂)₂ N, etc. are illustrated, and those kinds or two sorts or more of mixture is used.

[0019] As an organic solvent, ethylene carbonate, propylene carbonate, dimethyl carbonate, diethyl carbonate, ethyl methyl carbonate, dimethyl sulfoxide, a sulfolane, gamma-butyrolactone, 1, 2-dimethoxyethane, N.N-

dimethylformamide, a tetrahydrofuran, 1, 3-dioxolane, 2-methyl tetrahydrofuran, diethylether, etc. are illustrated, and those kinds or two sorts or more of mixture is used. Moreover, 1. is suitable for the concentration of the above-mentioned salts in the electrolytic solution in about 0.1-3 mols /.

[0020]

[Example] Hereafter, while an example explains this invention to a detail further, the example of comparison is also given and the remarkable effect of this invention is shown. %, the section and a certain **, and all mean weight % and the weight section below.

[0021] It is electrolysis MnO₂ as an example 1Mn raw material. It is Li₂ CO₃ as 78.2% and a Li raw material. 17.45%, It is nickel (OH)₂ as a nickel raw material. 0.84%, subsequently often mix those raw materials, using GeO as 3.51% and a germanium raw material, and at about 750 degrees C, calcinate the obtained mixture for about 15 hours, and, subsequently it is ground, respectively. Li(Mn1.90nickel0.08germanium0.02) O₄ The positive active material of the impalpable powder which consists of a spinel type Li-Mn system multiple oxide which has a chemical formula was obtained.

[0022] It is electrolysis MnO₂ as an example 2Mn raw material. It is Li₂ CO₃ as 78.2% and a Li raw material. 17.49%, It is nickel (OH)₂ as a nickel raw material. 1.68%, subsequently often mix those raw materials, using GeO as 2.63% and a germanium raw material, and at about 750 degrees C, calcinate the obtained mixture for about 15 hours, and, subsequently it is ground, respectively. Li(Mn1.90nickel0.06germanium0.04) O₄ The positive active material of the impalpable powder which consists of a spinel type Li-Mn system multiple oxide which has a chemical formula was obtained.

[0023] It is electrolysis MnO₂ as an example 3Mn raw material. It is Li₂ CO₃ as 78.22% and a Li raw material. 17.49%, It is nickel (OH)₂ as a nickel raw material. 2.1%, subsequently often mix those raw materials, using GeO as 2.19% and a germanium raw material, and at about 750 degrees C, calcinate the obtained mixture for about 15 hours, and, subsequently it is ground, respectively. Li(Mn1.90nickel0.05germanium0.05) O₄ The positive active material of the impalpable powder which consists of a spinel type Li-Mn system multiple oxide which has a chemical formula was obtained.

[0024] It is electrolysis MnO₂ as an example of comparison 1Mn raw material. It is Li₂ CO₃ as 78.14% and a Li raw material. 17.47%, Moreover, it is nickel (OH)₂ as a nickel raw material. Use 4.39%, respectively and subsequently often mix those raw materials, and at about 750 degrees C, calcinate the obtained mixture for about 15 hours, and, subsequently it is ground. Li(Mn1.90nickel0.1) O₄ The positive active material of the impalpable powder which consists of a spinel type Li-Mn system multiple oxide was obtained.

[0025] Each positive active material (particle to which all passed the Tyler screen of 330 meshes) of examples 1-3 and the example 1 of comparison was used, the positive-active-material 92 section, the acetylene black 3 section, the polyvinylidene-fluoride 5 section, and the N-methyl-2-pyrrolidone 70 section were mixed, and it considered as the slurry. This slurry is applied on an aluminum foil, and it dries, and is 20 mg/cm². The positive-electrode sheet which has a positive active material was produced. Adhesion opposite of each positive-electrode sheet and Li foil which were obtained in this way is carried out through porosity polyethylene separator, and it is one mol [per 11. (mixture a product ratio 1:1) of mixed solvents] LiPF₆ of ethylene carbonate and ethyl methyl carbonate. The solution which comes to dissolve was used as the electrolytic solution, this was sunk in between the above-mentioned positive-electrode sheet and Li foil, and the sealing coin type lithium secondary battery was produced.

[0026] The charge-and-discharge cycle examination was performed in the test method shown below about each lithium secondary battery. The result is shown in drawing 1 . In drawing 1 , 1-3 are the properties of each lithium secondary battery which used each positive active material of examples 1-3, respectively, and 4 is the property of the lithium secondary battery which used the positive active material of the example 1 of comparison.

[0027] Charge-and-discharge cycle test method: Set at 20 degrees C and it is 2 an area of 1cm of a positive-electrode sheet. It charges for 5 hours under the constant current and the constant voltage of 4.3V of 1mA of hits, and, subsequently is 2 an area of 1cm of a positive-electrode sheet. It is made to discharge until terminal voltage is set to 3V under the constant current of 0.5mA of hits, and charge and discharge are stopped after this for 1 hour. They are repeated 20 times, using the above charge and discharge and a pause as 1 cycle. The service capacity in each cycle computes quantity of electricity (mA-H) from a discharge current value and a charging time value, and obtains service capacity (mA-H/g) from the weight (g) of the positive active material contained in the lithium secondary battery.

[0028] As for drawing 1 , which lithium secondary battery which used each positive active material of examples 1-3 shows maintaining big service capacity in 20 times of charge-and-discharge cycles as contrasted with the lithium secondary battery which used the positive active material of the example 1 of comparison.

[0029]

[Effect of the Invention] The positive active material of this invention shows high service capacity as compared with the positive active material which consists of the conventional Li-Mn system multiple oxide, and, moreover, is extremely excellent also in the charge-and-discharge cycle property. Therefore, the positive active material of this

invention is suitable for manufacture of the long lasting lithium secondary battery for various kinds of electrical machinery and apparatus division portables.

[Translation done.]

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TECHNICAL FIELD

[The technical field to which invention belongs] Especially this invention relates to the positive active material for lithium secondary batteries which makes a principal component a spinel type Li-Mn system multiple oxide about the positive active material for lithium secondary batteries.

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PRIOR ART

[Description of the Prior Art] Generally the lithium secondary battery is attracting attention all the more because it is excellent in respect of electromotive force and the energy density, and various kinds of improvement researches for the purpose which develops a product with still higher practicality are made wholeheartedly in the field. Improvement research of a positive active material is also the one [important]. As a positive active material, instead of the multiple oxide (LiMeO₂ and Me are the new 9-10 group transition-metals element of a periodic table) of the conventional lithium and a transition-metals element, the spinel type Li-Mn multiple oxide (Li_AMn₂O₄) from which much more high electromotive force is obtained is proposed recently, and set to this multiple oxide. When the values of A are 0.05-0.5 and 4V class and the value of A are 0.5-1.1, it is known that a 3V class lithium secondary battery will be obtained.

[0003] By the way, the rechargeable battery using this Li-Mn multiple oxide as a positive active material has a problem in a charge-and-discharge cycle property generally. That is, if the cycle of charge and discharge is performed, the service capacity of a cell will fall rapidly. In order to improve this problem, replacing a part of Mn by elements, such as Co, Cr, nickel, and Fe, is proposed. However, even if this proposal is effective for an improvement of the charge-and-discharge cycle property of a cell, the new problem to which the service capacity per unit weight of a positive active material falls sharply is caused.

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EFFECT OF THE INVENTION

[Effect of the Invention] The positive active material of this invention shows high service capacity as compared with the positive active material which consists of the conventional Li-Mn system multiple oxide, and, moreover, is extremely excellent also in the charge-and-discharge cycle property. Therefore, the positive active material of this invention is suitable for manufacture of the long lasting lithium secondary battery for various kinds of electrical machinery and apparatus division portables.

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TECHNICAL PROBLEM

[Problem(s) to be Solved by the Invention] Carrying out a deer, this invention makes it a technical problem to propose a useful positive active material to manufacture of the lithium secondary battery excellent in both service capacity and the charge-and-discharge cycle property.

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MEANS

[Means for Solving the Problem] The above-mentioned technical problem is solvable with the positive active material for the following lithium secondary batteries.

- (1) The positive active material for lithium secondary batteries characterized by making into a principal component the spinel type Li-Mn system multiple oxide which has a general formula $\text{Li}_A \text{Mn}_x \text{Ni}_y \text{Ge}_z \text{O}_4$ (the atomic ratio of 0.02 to 0.4, and Y and Z is 1:9-9:1 here for the total quantity of $0.05 \leq A \leq 2.3$, $X+Y+Z=2$, and Y and Z).
- (2) the above (1) the general formula which can be set -- setting -- A -- 1 -- it is -- the total quantity of Y and Z -- 0.05-0.15 -- it is -- moreover, the atomic ratio of Y and Z -- 8(Y): -- 2 (Z) - 3(Y): -- the above (1) which is 7 (Z) Positive active material for the lithium secondary batteries of a publication.

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OPERATION

[Function] The above-mentioned technical problem is solvable by using what was replaced in the amount range of specification which is with nickel and germanium and describes above Mn of a spinel type Li-Mn system multiple oxide part as a positive active material.

[0007]

[Embodiments of the Invention] The spinel type Li-Mn system multiple oxide adopted by this invention has the following general formula (1). $LiA Mn_x Ni_y Ge_z O_4$ (1)

(For the total quantity of $0.05 \leq A \leq 2.3$, $X+Y+Z=2$, and Y and Z, the atomic ratio of 0.02 to 0.4, and Y and Z is 1:9-9:1 here).

[0008] (1) In an adult case, in a formula, there is a problem to which service capacity falls from the case where A value is less than 0.05, or 2.3. If [than 0.4] more [there are few improvement effects of service capacity and a charge-and-discharge cycle property that the total quantity of Y and Z is less than 0.02 and], it will become easy to generate impurity phases other than a spinel phase, and service capacity will decrease. Therefore, as for the total quantity of Y and Z, it is desirable the range of 0.03-0.3 and that it is especially the range of 0.05-0.15. In the atomic ratio of Y and Z, to it of Z, the improvement effect of service capacity has few atomic numbers of Y as it is excessive, and on the other hand, the atomic number of the improvement effect of a charge-and-discharge cycle property of Y decreases as too little to it of Z. therefore, the atomic ratio of Y and Z -- 8(Y): -- 2 (Z) - 3(Y): -- the range of 7 (Z) -- especially -- 7(Y): -- 3 (Z) - 4(Y): -- it is desirable that it is the range of 6 (Z)

[0009] if a desirable spinel type Li-Mn system multiple oxide is illustrated -- $Li(Mn1.90nickel0.08germanium0.02) O_4$, $Li(Mn1.90nickel0.06germanium0.04) O_4$, and $Li(Mn1.90nickel0.05germanium0.05) O_4$, $Li(Mn1.92nickel0.06germanium0.02) O_4$, and $Li(Mn1.92nickel0.05germanium0.03) O_4$ etc. -- it is .

[0010] Generally, the spinel type Li-Mn system multiple oxide shown by the general formula (1) can mix elements other than the oxygen which constitutes it, i.e., the oxide of Li, Mn, nickel, and germanium, a hydroxide, a carbonate, a nitrate, etc. so that the atomic ratio of each element may serve as a rate shown by (1) formula, and it can manufacture them by carrying out heating baking of the obtained mixture at 500-1000 degrees C in the atmosphere for 1- 50 hours. For example, it is $Li_2 CO_3$ considering electrolysis MnO_2 (EMD) as a Li raw material as a Mn raw material. Considering $LiOH \cdot H_2 O$ as a nickel raw material, it is nickel (OH)2. Moreover, using GeO respectively as a germanium raw material, subsequently, it can mix by the quantitative ratio of a request of those raw materials, and can manufacture by carrying out heating baking of the obtained mixture before and after 750 degrees C for about 15 hours. Moreover, $LiA Mn_2 O_4$ of the conventional common knowledge It can manufacture also by carrying out heating baking of the mixture of the multiple oxide which replaced a part of Mn only with nickel, and germanium raw materials, such as GeO , at 500-1000 degrees C in the atmosphere for 1 to 50 hours.

[0011] Even if the positive active material of this invention consists of a kind of the spinel type Li-Mn system multiple oxide shown by the general formula (1), or two sorts or more. It is good and you may use together with small quantity (for example, per [0.1] spinel type Li-Mn system multiple-oxide 100 weight section - 10 weight sections grade which are shown by the general formula (1)), such as various kinds of Li-Mn system multiple oxides other than the spinel type Li-Mn system multiple oxide shown by other positive active materials (1), for example, a general formula, if needed, and a Li-Co system multiple oxide.

[0012] The positive active material of this invention can use the conventional Li-Mn system multiple oxide by the same method as the method learned for fields made into a positive active material, such as a nonaqueous electrolyte lithium secondary battery and a solid electrolyte lithium secondary battery, from the former. Below, the example of some of the typical or desirable practical use method is explained.

[0013] As a binder of a positive active material, polytetrafluoroethylene, poly vinylidene fluoride, polyethylene, and ethylene-propylene-diene system polymer etc. is illustrated, and various conductive graphites, conductive carbon black, etc. are illustrated as an electric conduction agent.

[0014] The amount of the positive active material used is per [80] total quantity 100 weight section of a positive active material, a binder, and an electric conduction agent - 95 weight sections grade, and the amount of the binder

used is per [1] positive-active-material 100 weight section - 10 weight sections grade, and the amount of the electric conduction agent used is per [3] positive-active-material 100 weight section - 15 weight sections grade. [0015] A positive-electrode sheet applies the mixed constituent which becomes one side or both sides of a positive-electrode charge collector from a positive active material, a binder, and an electric conduction agent, fully, after dryness, it can roll out and form and what has an about 50-200-micrometer positive-active-material layer especially about 20-500 micrometers in thickness to one side or both sides is illustrated.

[0016] When an example desirable as a negative-electrode active material shared with the positive active material of this invention is given, it is graphites, such as a various kinds of natural-graphites and artificial graphites, for example, fibrous graphite, and scale-like graphite and a nodular graphite, and is polytetrafluoroethylene, poly vinylidene fluoride, polyethylene, and ethylene-propylene-diene system polymer etc. as the binder. The amount of the negative-electrode active material used is per [80] total quantity 100 weight section - 96 weight sections grade of a negative-electrode active material and a binder.

[0017] Especially especially as a positive-electrode charge collector, an about 30-150-micrometer expanded metal etc. is desirable about 25-300 micrometers in about 15-50-micrometer a foil and a fenestrate foil, and thickness about 10-100 micrometers in thickness of conductive metals, such as aluminum, an aluminium alloy, and titanium. Especially especially as a negative-electrode charge collector, an about 25-100-micrometer expanded metal etc. is desirable about 20-300 micrometers in about 8-50-micrometer a foil and a fenestrate foil, and thickness about 5-100 micrometers in thickness of conductive metals, such as copper, nickel, silver, and SUS.

[0018] As nonaqueous electrolyte, the electrolytic solution which dissolved salts in the organic solvent is illustrated. As these salts, LiClO₄, LiBF₄, LiPF₆, LiAsF₆, LiAlCl₄, Li(CF₃SO₂)₂N, etc. are illustrated, and those kinds or two sorts or more of mixture is used.

[0019] As an organic solvent, ethylene carbonate, propylene carbonate, dimethyl carbonate, diethyl carbonate, ethyl methyl carbonate, dimethyl sulfoxide, a sulfolane, gamma-butyrolactone, 1, 2-dimethoxyethane, N.N-dimethylformamide, a tetrahydrofuran, 1, 3-dioxolane, 2-methyl tetrahydrofuran, diethylether, etc. are illustrated, and those kinds or two sorts or more of mixture is used. Moreover, l. is suitable for the concentration of the above-mentioned salts in the electrolytic solution in about 0.1-3 mols /.

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EXAMPLE

[Example] Hereafter, while an example explains this invention to a detail further, the example of comparison is also given and the remarkable effect of this invention is shown. %, the section and a certain **, and all mean weight % and the weight section below.

[0021] It is electrolysis MnO₂ as an example 1Mn raw material. It is Li₂ CO₃ as 78.2% and a Li raw material. 17.45%, It is nickel (OH)₂ as a nickel raw material. 0.84%, subsequently often mix those raw materials, using GeO as 3.51% and a germanium raw material, and at about 750 degrees C, calcinate the obtained mixture for about 15 hours, and, subsequently it is ground, respectively. Li(Mn1.90nickel0.08germanium0.02) O₄ The positive active material of the impalpable powder which consists of a spinel type Li-Mn system multiple oxide which has a chemical formula was obtained.

[0022] It is electrolysis MnO₂ as an example 2Mn raw material. It is Li₂ CO₃ as 78.2% and a Li raw material. 17.49%, It is nickel (OH)₂ as a nickel raw material. 1.68%, subsequently often mix those raw materials, using GeO as 2.63% and a germanium raw material, and at about 750 degrees C, calcinate the obtained mixture for about 15 hours, and, subsequently it is ground, respectively. Li(Mn1.90nickel0.06germanium0.04) O₄ The positive active material of the impalpable powder which consists of a spinel type Li-Mn system multiple oxide which has a chemical formula was obtained.

[0023] It is electrolysis MnO₂ as an example 3Mn raw material. It is Li₂ CO₃ as 78.22% and a Li raw material. 17.49%, It is nickel (OH)₂ as a nickel raw material. 2.1%, subsequently often mix those raw materials, using GeO as 2.19% and a germanium raw material, and at about 750 degrees C, calcinate the obtained mixture for about 15 hours, and, subsequently it is ground, respectively. Li(Mn1.90nickel0.05germanium0.05) O₄ The positive active material of the impalpable powder which consists of a spinel type Li-Mn system multiple oxide which has a chemical formula was obtained.

[0024] It is electrolysis MnO₂ as an example of comparison 1Mn raw material. It is Li₂ CO₃ as 78.14% and a Li raw material. 17.47%, Moreover, it is nickel (OH)₂ as a nickel raw material. Use 4.39%, respectively and subsequently often mix those raw materials, and at about 750 degrees C, calcinate the obtained mixture for about 15 hours, and, subsequently it is ground. Li(Mn1.90nickel0.1) O₄ The positive active material of the impalpable powder which consists of a spinel type Li-Mn system multiple oxide was obtained.

[0025] Each positive active material (particle to which all passed the Tyler screen of 330 meshes) of examples 1-3 and the example 1 of comparison was used, the positive-active-material 92 section, the acetylene black 3 section, the polyvinylidene-fluoride 5 section, and the N-methyl-2-pyrrolidone 70 section were mixed, and it considered as the slurry. This slurry is applied on an aluminum foil, and it dries, and is 20 mg/cm². The positive-electrode sheet which has a positive active material was produced. Adhesion opposite of each positive-electrode sheet and Li foil which were obtained in this way is carried out through porosity polyethylene separator, and it is one mol [per 11. (mixture a product ratio 1:1) of mixed solvents] LiPF₆ of ethylene carbonate and ethyl methyl carbonate. The solution which comes to dissolve was used as the electrolytic solution, this was sunk in between the above-mentioned positive-electrode sheet and Li foil, and the sealing coin type lithium secondary battery was produced.

[0026] The charge-and-discharge cycle examination was performed in the test method shown below about each lithium secondary battery. The result is shown in drawing 1 . In drawing 1 , 1-3 are the properties of each lithium secondary battery which used each positive active material of examples 1-3, respectively, and 4 is the property of the lithium secondary battery which used the positive active material of the example 1 of comparison.

[0027] Charge-and-discharge cycle test method: Set at 20 degrees C and it is 2 an area of 1cm of a positive-electrode sheet. It charges for 5 hours under the constant current and the constant voltage of 4.3V of 1mA of hits, and, subsequently is 2 an area of 1cm of a positive-electrode sheet. It is made to discharge until terminal voltage is set to 3V under the constant current of 0.5mA of hits, and charge and discharge are stopped after this for 1 hour. They are repeated 20 times, using the above charge and discharge and a pause as 1 cycle. The service capacity in each cycle computes quantity of electricity (mA-H) from a discharge current value and a charging time value, and obtains service capacity (mA-H/g) from the weight (g) of the positive active material contained in the lithium

secondary battery.

[0028] As for drawing 1 , which lithium secondary battery which used each positive active material of examples 1-3 shows maintaining big service capacity in 20 times of charge-and-discharge cycles as contrasted with the lithium secondary battery which used the positive active material of the example 1 of comparison.

[Translation done.]

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DESCRIPTION OF DRAWINGS

[Brief Description of the Drawings]

[Drawing 1] It is the graph which shows the charge-and-discharge cycle property of each lithium secondary battery which used each positive active material of the examples 1-3 of this invention, and the example 1 of comparison.

[Description of Notations]

- 1 It is the property of the lithium secondary battery which used the positive active material of an example 1.
- 2 It is the property of the lithium secondary battery which used the positive active material of an example 2.
- 3 It is the property of the lithium secondary battery which used the positive active material of an example 3.
- 4 It is the property of the lithium secondary battery which used the positive active material of the example 1 of comparison.

[Translation done.]

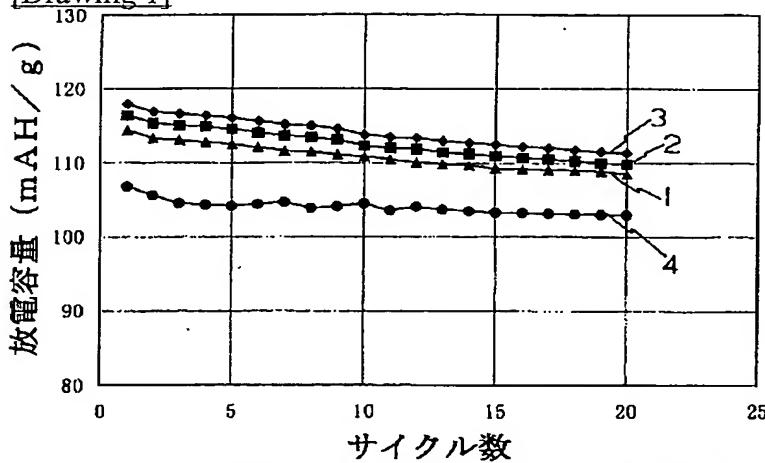
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DRAWINGS

[Drawing 1]



- 1 実施例 1 の正極活性物質を使用したリチウム二次電池の特性
- 2 実施例 2 の正極活性物質を使用したリチウム二次電池の特性
- 3 実施例 3 の正極活性物質を使用したリチウム二次電池の特性
- 4 比較例 1 の正極活性物質を使用したリチウム二次電池の特性

[Translation done.]